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ECBC-TR-336

HYDROLYSIS OF LEVINSTEIN MUSTARD (H)

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August 2003

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20031217 035

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Aberdeen Proving Ground, MD 21010-5424

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	2003 August	Final; 02 Oct – 03 Mar

4. TITLE AND SUBTITLE

Hydrolysis of Levinstein Mustard (H)

5. FUNDING NUMBERS

None

6. AUTHOR(S)

Rohrbaugh, Dennis, K.; Wagner, George, W.; Sumpter Kenneth, B.; and Harvey, Steven, P.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

DIR, ECBC, ATTN: AMSSB-RRT-AC, APG, MD 21010-5424

8. PERFORMING ORGANIZATION REPORT NUMBER

ECBC-TR-336

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Samples of Levinstein mustard (H) were removed from leaking munitions. These samples were labeled "liquid" and "solid," although both samples contained materials of both phases. The samples were analyzed by gas chromatography/mass spectrometry (GC/MS) and were found to contain HD as a minor component in both cases. The liquid sample was analyzed by ^{13}C nuclear magnetic resonance (NMR) and was found to contain thiodiglycol as the single most abundant compound. Liquid and solid samples were hydrolyzed at a concentration of 15% H in water, with subsequent addition of an excess of NaOH. The hydrolysates were extracted with either chloroform, hexane, or cyclohexane and analyzed by GC/MS and in all cases were found to contain no HD at or above the drinking water level of 200 ppb. The GC/MS analysis of the solid sample showed a number of cyclic compounds not found in the liquid hydrolysate. In general, cyclohexane was found to be the preferred solvent for extraction because it provided a better NMR matrix than either hexane or chloroform and cleanly separated the extract from the large mass of high density solids on the bottom of the extract.

14. SUBJECT TERMS

Levinstein mustard (H)	GC/MS
Hydrolysis	NMR

15. NUMBER OF PAGES

19

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

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PREFACE

The work described in this report was authorized by the Program Manager for Assembled Chemical Weapons Assessment. This work was started in October 2002 and completed in March 2003.

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Acknowledgment

The authors acknowledge the Assembled Chemical Weapons Assessment Program for funding this work.

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HYDROLYSIS OF LEVINSTEIN MUSTARD (H)

1. INTRODUCTION

A portion of the U.S. chemical stockpile consists of H, or Levinstein mustard. The Levinstein process is a low temperature (30 °C) process for synthesizing relatively crude mustard, primarily for use in weapons. Mustard is produced by the addition of sulfur dichloride to ethylene to form 2-chloroethylsulfenyl chloride (1) and the addition of that compound to a second molecule of ethylene (2).*

$$SCl_2 + CH_2{=}CH_2 \rightarrow ClCH_2CH_2SCl \qquad (1)$$

$$ClCH_2CH_2SCl + CH_2{=}CH_2 \rightarrow S(CH_2CH_2Cl)_2 \qquad (2)$$

The process was first described in England** and was based on the observation that very pure ethylene is absorbed rapidly by sulfur monochloride in the presence of crude mustard at temperatures as low as 30 °C. The primary industrial advantage of this approach was that it avoided the mustard decomposition and sulfur precipitation associated with the high temperature (typically 60 °C) synthesis and subsequent vacuum distillation processes used previously.

Briefly, pure ethylene chloride was passed into a reactor partly filled with the product from a former run, while sulfur monochloride was also fed in. The critical aspect was the maintenance of the proper concentration of sulfur monochloride. When the reactor was nearly full, the sulfur monochloride feed was shut off and the product was completely saturated with ethylene. The major portion of the product was then drawn off and the cycle repeated. Using this process, 30 tons of mustard per day were produced in Edgewood, MD, starting November 1, 1918.

For the purposes of this study, two H samples were used. One sample was labeled "liquid" and one sample was labeled "solid", although it should be emphasized both samples contained materials of both phases; there was no clear demarcation between the two sample types. Both were greenish-black in color. The liquid sample contained small (typically several millimeters in diameter) solid particles in suspension, while the solid sample was actually a semi-solid, which although it did not pour well, still adapted to the shape of its container.

2. MATERIALS AND METHODS

The H liquid (400 mL) and H solids (495.9 g) samples were received at the U.S. Army Edgewood Chemical Biological Center (ECBC) from the Chemical Agent Munitions Destruction System (CAMDS), Utah, November, 2002. The material had originally been removed from old, leaking munitions, stored for several years in a container. The H sample was predominantly liquid, greenish in color, with small black solids suspended in it, and was labeled 51-02. The solid was of similar color, but with relatively more solid material and containing relatively less liquid. It was also labeled 51-02. Aliquots were removed from one of the solids containers and one of the liquid containers for analysis. Neither sample was homogeneous and although the aliquots removed were as representative as possible, the viscous and biphasic nature of the material precluded a thoroughly representative sampling.

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* National Academy Press, Veterans at Risk, Chapter 5: Chemistry of Sulfur Mustard and Lewisite, pp. 71-72. National Academy Press, 1993.

** Organic Chemistry of Bivalent Sulfur, Vol. II, by E. Emmet Reid, Chapter 5. Mustard Gas, p237 to 288, Chemical Publishing Co., Inc, NY, NY, 1960.

3. RESULTS

3.1 Analysis of Starting Materials.

3.1.1 GC/MS Analysis of H Liquid.

Approximately 20 mg of each H sample was partially dissolved in about 0.4 mL acetonitrile (a portion of each sample remained as a dark brown residue). Samples appeared to be insoluble in methylene chloride and terahydrofuran. Acetonitrile solutions were analyzed by gas chromatography/mass spectrometry (GC/MS) using a Hewlett-Packard HP5972 MSD. Conditions were as follows:

Column: 25 m x 0.25 mm Rtx5-ms, 0.25 μm film (Restek, Bellefonte, PA)
Column temperature: 60 °C, 15 °C/min to 280 °C, 5 min at 280 °C
Injection mode: Split 20:1
Injection volume: 0.5 μL manual injection
Injection temperature: 250 °C
Interface temperature: 280 °C
Source temperature: 150 °C
Scan range: 40-450 Da
Scan time: 0.545 s
Electron Energy: 70 eV

The results the GC/MS analysis of ACWA H-52-02-01 are listed below in Table 1.

Table 1. GC/MS Analysis of ACWA H-52-02-01

Date samples received: 20 November 2002
Date samples analyzed: 20 November 2002
Appearance: Yellowish-green liquid (NMR Tube)
Method: Liquid partially dissolved in acetonitrile and derivatized 1:1 with BSTFA for 30 min at 60 °C

RT (min)	Compound	Area %
3.11	1,4-Thioxane	25.1
3.79	$HOCH_2CH_2OH$*	3.6
4.86	1,4-Dithiane	12.5
5.87	HD	0.9
6.88	$HOCH_2CH_2SCH_2CH_2Cl$*	17.8
7.91	Thiodiglycol*	34.3
10.90	$HOCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$*	2.8
11.49	$HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$*	0.3
	Unidentified (3 peaks)	2.8

*Detected as trimethylsilyl derivative.
Quantitation is by GC/MS area percent and represents only an approximation.
GC Conditions: 30m x 0.25mm Rtx-5 column; 60-270 °C @ 15 °C/min, 270 °C for 10 min

3.1.2 GC/MS Analysis of H Solids.

The analysis of ACWA H-52-02-05 are listed below in Table 2.

Table 2. GC/MS Analysis of ACWA H-52-02-05

Date samples received: 21 November 2002
Date samples analyzed: 21 November 2002
Appearance: Dark brown solid paste
Method: Solid partially dissolved in acetonitrile and derivatized 1:1 with BSTFA for 30 min at 60 °C

RT (min)	Compound	Area %
3.18	1,4-Thioxane	17.2
3.83	$HOCH_2CH_2OH$*	0.7
4.90	1,4-Dithiane	28.9
5.88	HD	1.6
6.24	$ClCH{=}CHSCH_2CH_2Cl$ or isomer	0.2
6.91	$HOCH_2CH_2SCH_2CH_2Cl$*	13.4
7.84	1,2,5-Trithiepane	0.3
7.93	Thiodiglycol*	20.0
8.22	1-Oxa-4,7-dithionane	0.7
9.92	HD trisulfide	0.9
10.11	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2OH$*	0.4
10.35	Q	0.5
10.92	$HOCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$*	3.3
11.51	$HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$*	0.7
12.83	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2Cl$*	2.2
13.28	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	2.3
	Unidentified (11 peaks)	6.7

*Detected as trimethylsilyl derivative.
Quantitation is by GC/MS area percent and represents only an approximation.
GC Conditions: 30m x 0.25mm Rtx-5 column; 60-270 °C @ 15 °C/min, 270 °C for 10 min

3.2 Hydrolysis Reactions.

3.2.1 Hydrolysis of 15% Liquid H in Water, Followed by Neutralization with NaOH.

3.2.1.1 15% Reaction #1.

Water (85 g) was placed in a water-jacketed vessel (total capacity 250 mL) and heated to approximately 90 °C. Agitation was provided by a 1-in. stir bar with the magnetic stirrer operated at full speed. Liquid H (15 g) was added batchwise and agitated at temperature for 1 hr. The solution was cooled to room temperature, and NaOH (10 g) was added to the resulting hydrolysate and stirred for a few minutes to ensure dissolution. This material was extracted with 10% chloroform by volume. The extract was

centrifuged, which caused the considerable solid fraction to precipitate in the tube. The total liquid fraction was decanted and centrifuged again to separate the chloroform layer from the aqueous layer. Less than 1 mL of chloroform was subsequently recovered in the bottom of the tube. This material was submitted for analysis to determine the concentration of residual mustard, if any. According to the following analytical report, no Levinstein H was found above the drinking water level of of 0.2µg H/mL of Reaction Product.

Analytical Report

TITLE: GC/MSD Analysis of Chloroform Extract of 15% Levinstein Mustard Reaction Product.

TO: Dr. Steve Harvey
ATTN: AMSSB-RRT-BT

FROM Kenneth Sumpter
ATTN: AMSSB-RRT-PC

DATE OF RECEIPT OF SAMPLE: 26 November 2002

DATE OF ANALYSES: 27 November 2002

NAME OF ANALYSTS: Kenneth Sumpter

TEST METHOD: HD Delisting

GC/MSD Parameters

GC Condition		HP 5972 MSD Conditions	
Initial Oven Temp. (°C)	60	Solvent Delay	6.00
Initial Oven Time (min.)	3.00	Detector Temp (°C)	280
Rate (°C/min)	10	Mode	Selected Ion
Final Oven Temp. (°C)	260	Ion Group	63, 109, 111, 123, 158
Injection Temp. (°C)	250		
Purge Time On (min)	0.5		
Injection Volume (µL)	1		

RESULTS:

A 10:1 chloroform extract was received from Dr. Harvey on 26 November 2002. Sample was analyzed by GC/MSD in the selected ion mode and was found to contain no Levinstein H above the drinking water level of 0.2 µg H/mL of Reaction Product.

Retention time and reference mass spectra were obtained for HD by analyzing 2 µg/mL HD/$CHCL_3$ and a 2 µg/mL HD post spike of the n-hexane extract.

/s/ KENNETH B. SUMPTER
AGENT CHEMISTRY TEAM

3.2.1.2 15% Reaction #2.

This reaction was performed in the same manner as 15% reaction #1 above. Extraction was with hexane (10 mL hexane into 40 mL hydrolysate). This provided a much simpler extraction procedure as the hexane formed a clear upper layer and was thus distinct from the solids that precipitated to the bottom during centrifugation. According to the following analytical report, no Levinstein H was found above the drinking water level of 0.2µg H/mL of Reaction Product.

Analytical Report

TITLE: GC/MSD Analysis of n-Hexane Extract of 15% Levinstein Mustard Reaction Product.

TO: Dr. Steve Harvey
ATTN: AMSSB-RRT-BT

FROM Kenneth Sumpter
ATTN: AMSSB-RRT-PC

DATE OF RECEIPT OF SAMPLE: 02 December 2002

DATE OF ANALYSES: 3 – 4 December 2002

NAME OF ANALYSTS: Kenneth Sumpter

TEST METHOD: HD Delisting

GC/MSD Parameters

GC Condition		HP5972 MSD Conditions	
Initial Oven Temp. (°C)	60	Solvent Delay	6.00
Initial Oven Time (min.)	3.00	Detector Temp (°C)	280
Rate (°C/min)	10	Mode	Selected Ion
Final Oven Temp. (°C)	260	Ion Group	63, 109, 111, 123, 158
Injection Temp. (°C)	250		
Purge Time On (min)	0.5		
Injection Volume (µL)	1		

RESULTS:

A 10:2 n-hexane extract was received from Dr. Harvey on 02 December 2002. Sample was analyzed by GC/MSD in the selected ion mode and was found to contain no Levinstein H above the drinking water level of 0.2 µg H/mL of Reaction Product.

Retention time and reference mass spectra were obtained for HD by analyzing 2 µg/mL HD/$CHCL_3$ and a 2 µg/mL HD post spike of the n-hexane extract.

/s/ KENNETH B. SUMPTER
AGENT CHEMISTRY TEAM

3.2.1.3 15% Reaction #3.

This reaction was performed in the same manner as the previous two reactions. Extraction was the same as with reaction #2 above, plus a cyclohexane extract was included. According to the following analytical reports, no Levinstein H was found above the drinking water level of of 0.2 µg H/mL of Reaction Product in either extract.

Analytical Report

TITLE: GC/MSD Analysis of n-Hexane Extract of 15% Levinstein Mustard Reaction Product.

TO: Dr. Steve Harvey
ATTN: AMSSB-RRT-BT

FROM Kenneth Sumpter
ATTN: AMSSB-RRT-PC

DATE OF RECEIPT OF SAMPLE: 19 December 2002

DATE OF ANALYSES: 20 December 2002

NAME OF ANALYSTS: Kenneth Sumpter

TEST METHOD: HD Delisting

GC/MSD Parameters

GC Condition		HP5972 MSD Conditions	
Initial Oven Temp. (°C)	60	Solvent Delay	6.00
Initial Oven Time (min.)	3.00	Detector Temp (°C)	280
Rate (°C/min)	10	Mode	Selected Ion
Final Oven Temp. (°C)	260	Ion Group	109, 111, 123, 158, 160
Injection Temp. (°C)	250		
Purge Time On (min)	0.5		
Injection Volume (µL)	1		

RESULTS:

A 10:2 n-hexane extract was received from Dr. Harvey on 19 December 2002. Sample was analyzed by GC/MSD in the selected ion mode and was found to contain no Levinstein H above the drinking water level of 0.2 µg H/mL of Reaction Product.

Retention time and reference mass spectra were obtained for HD by analyzing 0.93 µg/mL HD/$CHCL_3$ and a 0.93 µg/mL HD pre-spike of the aqueous reaction product.

Mass to charge 63 was not used as one of the selected ions due to considerable amount of background. Mass to charge 160 replaced the m/z 63.

/s/ KENNETH B. SUMPTER
AGENT CHEMISTRY TEAM

Analytical Report

TITLE: GC/MSD Analysis of Cyclohexane Extract of 15% Levinstein Mustard Reaction Product.

TO: Dr. Steve Harvey
ATTN: AMSSB-RRT-BT

FROM Kenneth Sumpter
ATTN: AMSSB-RRT-PC

DATE OF RECEIPT OF SAMPLE: 19 December 2002

DATE OF ANALYSIS: 20 December 2002

NAME OF ANALYST: Kenneth Sumpter

TEST METHOD: HD Delisting

GC/MSD Parameters

GC Condition		HP5973 MSD Conditions	
Initial Oven Temp. (°C)	60	Solvent Delay	6.00
Initial Oven Time (min.)	3.00	Detector Temp (°C)	280
Rate (°C/min)	10	Mode	Selected Ion
Final Oven Temp. (°C)	260	Ion Group	109, 111, 123, 158, 160
Injection Temp. (°C)	250		
Purge Time On (min)	0.5		
Injection Volume (µL)	1		

RESULTS:

A 10:2 cyclohexane extract was received from Dr. Harvey on 19 December 2002. Sample was analyzed by GC/MSD in the selected ion mode and was found to contain no Levinstein H above the drinking water level of 0.2 µg H/mL of Reaction Product.

Retention time and reference mass spectra were obtained for HD by analyzing 0.93 µg/mL HD/n-hexane.

Mass to charge 63 was not used as one of the selected ions due to considerable amount of background. Mass to charge 160 replaced the m/z 63.

/s/ KENNETH B. SUMPTER
AGENT CHEMISTRY TEAM

3.3 Detailed Analyses of Reaction Products.

3.3.1 GC/MS Analysis of 15% Liquid Hydrolysate (Dried and Derivatized Products of Reaction 2).

The results of the GC/MS analysis of 15% liquid hydrolysate are listed below in Table 3.

Table 3. GC/MS Analysis of 15% Liquid Hydrolysate (Dried and Derivatized Products of Reaction 2)

Date samples received: 12 December 2002
Date samples analyzed: 12 December 2002
Appearance: Dark brown suspension
Method: 0.05 mL evaporated to dryness and derivatized with 0.05 mL BSTFA for 30 min/60 °C

RT (min)	Compound	Area %
3.82	$HOCH_2CH_2OH$*	39.1
3.94	$HOCH_2CH_2CH_2OH$*	0.08
4.34, 4.68	$HOCH_2CH_2CH_2CH_2OH$* Isomers	0.16
4.69	$CH_2{=}CHSCH_2CH_2OH$*	0.12
4.87	1,4-Dithiane	0.01
6.32	$HOCH_2CH_2OCH_2CH_2OH$*	0.4
7.93	Thiodiglycol*	42.2
8.30, 8.38, 8.67	$HOCH_2CH_2CH_2CH_2SCH_2CH_2OH$* Isomers	0.3
8.98	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OH$*	2.7
10.09	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2OH$*	2.8
11.49	$HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$*	3.7
13.27	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	8.6

*Detected as trimethylsilyl derivative.
Quantitation is by GC/MS area percent and represents only an approximation.
GC Conditions: 30m x 0.25mm Rtx-5 column; 60-270 °C @ 15 °C/min, 270 °C for 10 min

3.3.2 GC/MS Analysis of ACWA H Liquid Hydrolysate (15%, rxn 3) 10:2 Hexane Extract.

The results of the GC/MS analysis of ACWA H liquid hydrolysate are listed below in Table 4.

Table 4. GC/MS Analysis of ACWA H Liquid Hydrolysate (15%, rxn 3) 10:2 Hexane Extract

Date samples received: 12 December 2002
Date samples analyzed: 13 December 2002
Appearance: Clear, colorless liquid
Method: 0.05 mL evaporated to dryness and derivatized with 0.05 mL BSTFA for 30 min/60 °C

RT (min)	Compound	Area %
3.18	1,4-Thioxane	26.8
4.02, 4.29, 4.41	cyclic $-OCH_2CH_2CH_2CH_2SCH_2CH_2-$ isomers	
4.71	$CH_2{=}CHSCH_2CH_2OH$*	1.5
4.90	1,4-Dithiane	32.7
5.72	$CH_2{=}CHSCH_2CH_2SCH{=}CH_2$	3.6
5.87	cyclic $-SCH_2CH_2CH_2CH_2SCH_2CH_2-$	0.6
8.21	cyclic $-OCH_2CH_2SCH_2CH_2SCH_2CH_2-$	0.08
9.00	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OH$*	24.1
10.83	cyclic $-OCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2-$	0.8
11.18	$CH_2{=}CHSCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	0.9
12.29	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OCH_2CH_2SCH{=}CH_2$	1.6
14.30	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	1.7
15.44	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2SCH{=}CH_2$	2.9

*Detected as trimethylsilyl derivative.
Quantitation is by GC/MS area percent and represents only an approximation.
GC Conditions: 30m x 0.25mm Rtx-5 column; 60-270 °C @ 15 °C/min, 270 °C for 10 min

3.3.3 GC/MS Analysis of ACWA H Solid Hydrolysate (15%) 10:2 Hexane Extract.

The results of the GS/MS analysis of ACWA H solid hydrolysate are listed below in Table 5.

Table 5. GC/MS Analysis of ACWA H Solid Hydrolysate (15%) 10:2 Hexane Extract

Date samples received: 17 December 2002
Date samples analyzed: 17 December 2002
Appearance: Clear, colorless liquid
Method: 0.05 mL evaporated to dryness and derivatized with 0.05 mL BSTFA for 30 min/60 °C

RT (min)	Compound	Area %
3.16	1,4-Thioxane	3.7
4.69	CH_2=$CHSCH_2CH_2OH$*	0.3
4.88	1,4-Dithiane	39.5
5.72	CH_2=$CHSCH_2CH_2SCH$=CH_2	0.3
7.83	cyclic –$SCH_2CH_2SSCH_2CH_2$-	0.11
7.91	Thiodiglycol*	0.02
8.20	cyclic -$OCH_2CH_2SCH_2CH_2SCH_2CH_2$-	0.2
8.99	CH_2=$CHSCH_2CH_2SCH_2CH_2OH$*	39.0
10.81	cyclic -$OCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2$-	1.9
11.16	CH_2=$CHSCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	2.1
12.38	cyclic -$SCH_2CH_2SCH_2CH_2SCH_2CH_2OCH_2CH_2$-	0.07
12.58	Unknown	0.5
14.16	cyclic -$SCH_2CH_2SCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2$-	0.3
14.29	CH_2=$CHSCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	12.1

*Detected as trimethylsilyl derivative.
Quantitation is by GC/MS area percent and represents only an approximation.
GC Conditions: 30m x 0.25mm Rtx-5 column; 60-270 °C @ 15 °C/min, 270 °C for 10 min

3.3.4 GC/MS Analysis of ACWA H Solid Hydrolysate (15%).

The results of the GS/MS analysis of ACWA H solid hydrolysate are listed below in Table 6.

Table 6. GC/MS Analysis of ACWA H Solid Hydrolysate (15%)

Date samples received: 17 December 2002
Date samples analyzed: 18 December 2002
Appearance: Dark brown mud
Method: 0.05 mL evaporated to dryness and derivatized with 0.05 mL BSTFA for 30 min/60 °C. Some of the residue was not soluble in the derivatizing agent.

RT (min)	Compound	Area %
3.14	1,4-Thioxane	4.6
3.80	$HOCH_2CH_2OH$*	11.2
4.68	$CH_2{=}CHSCH_2CH_2OH$*	0.9
4.86	1,4-Dithiane	1.6
6.90	Unknown	1.2
7.90	Thiodiglycol*	46.4
8.97	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OH$*	18.5
10.09	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2OH$*	1.2
11.48	$HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$*	3.4
13.26	$HOCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	8.7
14.29	$CH_2{=}CHSCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OH$*	1.9
16.16	Isomer of RT 14.29 min	0.4

*Detected as trimethylsilyl derivative.
Quantitation is by GC/MS area percent and represents only an approximation.
GC Conditions: 30m x 0.25mm Rtx-5 column; 60-270 °C @ 15 °C/min, 270 °C for 10 min

3.3.5 NMR Analysis of H and H Solid Hydrolysates/Hexane and Cyclohexane Extracts.

The NMR spectra were obtained using a Varian Unityplus 300 NMR spectrometer. Both 1H and 13C were attempted, with varying success.

(1) H 15% Hydrolysate - black material settled out; only ran clear, upper layer.

1H: Peaks too broad to be of use.

13C: Good data obtained; peaks assigned based on GC/MS results; sample spiked with 1,4-thioxane to confirm assignment and allow wt% calculation. Results for the H 15% Hydrolysate are (GC data given for comparison):

Compound	Wt %	Mol %	GC/MS Area %
TG	3.1	50.0	42.2
EG	1.2	37.3	39.1
TOH	0.98	8.5	8.6
1,4-thioxane	0.22	4.2	N.D.
Totals	5.5%	100.0%	89.9%

(2) H 15% Hydrolysate, Hexane Extract - good spectra (both 1H and 13C) obtained for hexane, but except for one of the 1,4-thioxane peaks, the compounds of interest were occluded by the intense, multiple hexane peaks.

(3) H Solid 15% Hydrolysate - black viscous material; did not separate. No peaks observed for this mud in either 1H or 13C.

(4) H Solid 15% Hydrolysate, Hexane Extract - same as 2) above.

(5) H Solid 15% hydrolysate, cyclohexane extract.

Cyclohexane, possessing only a single carbon peak, provided a better vista to detect compounds, but 1,4-dithiane was the only other compound found (besides 1,4-thioxane which was easily seen in the hexane extract). Results for the cyclohexane extract of the H Solids 15% hydrolysate are (sample weight 0.7g):

Compound	μmol	wt (mg)	wt % in sample
1,4-thioxane	23.0	2.40	0.34
1,4-dithiane	52.5	6.31	0.90

4. CONCLUSIONS

- The HD comprised only a minor component of the liquid and solid H samples.

- The other products identified were various HD-related breakdown products and impurities.

- Hydrolysis reactions conducted with 15% H in water with subsequent NaOH addition yielded no H levels at or above the drinking water level. This result held true for three successive reactions extracted with chloroform, hexane, or cyclohexane.

- The GC/MS analysis of the liquid H hydrolysate revealed a series of alcoholic compounds.

- The GC/MS analysis of the solid sample hydrolysate revealed a number of cyclic compounds in addition to several similar to those found in the liquid hydrolysate.

- The nuclear magnetic resource (NMR) analysis was performed on the clear, upper layer of the 15% liquid hydrolysate. The ^{1}H analysis revealed peaks too broad to be useful. The ^{13}C analysis yielded good data. Peaks were assigned based on GC/MS results; sample was spiked with thioxane to confirm assignment and allow weight percent calculations. Thiodiglycol was the single most abundant compound (42.2 area percent).

- Solid hydrolysate yielded no useful information with either ^{1}H or ^{13}C NMR (hydrolysate was a black, viscous material that did not separate).

- The NMR analysis of the cyclohexane extract of the H solid hydrolysate yielded 1,4-thioxane and 1,4-dithiane only.

- For the purposes of NMR analysis, the cyclohexane extract provided a better matrix than hexane or chloroform. For purposes of extraction, either hexane or cyclohexane were preferable to chloroform because the less dense alkanes formed a clear layer on the top of the extract, whereas the chlorinated solvent layered on the bottom of the extract and was mixed with a large mass of high density solids.